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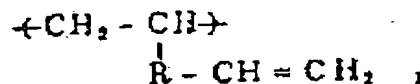
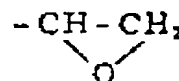
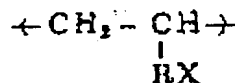
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(54) EPOXY GROUP-CONTAINING COPOLYMER

(57)Abstract:

PURPOSE: To obtain a new epoxy group-containing ethylene copolymer having a wide use because of excellent reactivity to amine compound, adhesivity to various materials, excellent properties as compatibilizing agent, etc., comprising a specific structure containing an epoxy group at the end of branched chain.
 CONSTITUTION: The objective copolymer comprising an ethylene unit shown by the formula $-(CH_2-CH_2)-$ and a unit shown by formula I (R is $\geq 4C$ straight-chain alkylene; X is $CH=CH_2$ group or group shown by formula II), containing 0.2-20 mol % unit shown by formula I wherein ≥ 1 % group X in the unit shown by formula I is group shown by formula II. The copolymer, for example, is obtained by epoxidizing ≥ 1 % end unsaturated group of side chain of unsaturated copolymer comprising an ethylene unit and 0.2-20 mol % α, ω -nonconjugated diene unit shown by formula III by oxidation with peracetic acid. 1,7-Octadiene is used as the α, ω -nonconjugated diene to provide the unit shown by formula III.



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English Translation of JP 04-055403 A

* NOTICES *

1. This document has been translated by computer using translation software. PAT-Transer V7 produced by Cross Language Inc. So the translation may not reflect the original precisely.
 2. The word which can not be translated is expressed by Japanese character.
 3. The drawings and tables are not translated.
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2. claims

(1) (A) An ethylene unit: $\text{---CH}_2\text{---CH}_2\text{---}$ extends

(B) The next expression (I)

(during a ceremony, R expresses linear alkylene group more than number of carbon atom 4 X expresses the ---CH=CH_2 basis or the basis.)

Be copolymer including the unit that it attends, and is expressed,

(B) 0.2-20 mol % contains a unit,

(B) The ethylene copolymer which contains epoxy function on the end of the side-chain that more than 1% of basis X of a unit are the $\text{---CH}_2\text{---CH}_2\text{---}$ bases.

(2) Copolymer, more, of a small quantity

It is a α -olefin unit (C): $\text{---CH}_2\text{---CH(R)---}$ (R expresses number of carbon atom 1 - ten alkyl groups).

Ethylene copolymer as claimed in 1 to include.

3. detailed description of the invention

(a field of industrial application)

The present invention is related to new ethylene copolymer containing the epee Kishi basis on the end of side-chain.

(prior art)

Ethylene, homopolymer of olefin such as propylene or copolymer is utilized in various field by the superior physical property and compactibility. However, it is poor, and character such as adhesive property or printing appropriateness is remarkable, and olefin polymer is inferior to an affinity with other materials from the place where molecular structure is nonpolar. In addition, if various, polar character structure including engineering plastic is blended with lasting resin, even if it is done in case, miscibility has shortcoming to be bad.

For example, for olefin polymer, maleic anhydride, vinyl acetate, acrylic acid, the method how grafting denatures metalllyl oate or the method how copolymerization does olefin and polar group component monomer is suggested a radical polymerizable compound owning polar group in an existence bottom of a radical generant to make up for these shortcoming. As for the property modification polymer produced by these methods, it becomes considerably of practical use. However, in late years advancement of the characteristic properties and diversification of field of application are demanded for resin materials remarkably, new

degeneration polymer having various function which can be applied to it becomes need.

The unsaturation copolymer resin that it is from 1,4- dienes of α - olefin and particular configuration to Japanese Patent Laid-Open No. 61-85405 as one of the property modification polymer of this field is denatured, the degeneration copolymer which epoxy function was introduced into by the end of the resin is disclosed.

However, epoxy function in this property modification copolymer is based on structure of the 1,4- dienes , for example, reactivity is bad, and basic compound is particularly inferior in ability as modified resin for amine compound and amine group component polymer so that there is in the inside of carbon chain, application field has shortcoming to be small.

(a problem to be solved by the invention)

The present invention was made in view of such present conditions , as compared with conventional property modification ethylene copolymer, that superior ethylene copolymer is provided in functionality more is done with the problem.

(a means for solving problem)

The present invention,

(A) It is an ethylene unit: \blacksquare CH₂-CH₂ \blacksquare extends

(B) The next expression (I)

(during a ceremony, R expresses linear alkylene group more than number of carbon atom 4 X expresses the \cdot CH = CH₂ basis or the $\blacksquare\blacksquare$ basis.)

Be copolymer including the unit that it attends, and is expressed,

(B) 0.2-20 mol % contains a unit,

(B) More than 1% of basis X of a unit

Ethylene copolymer containing epoxy function on the end of the side-chain which is the basis is related to.

Furthermore, the present invention is an ethylene unit again

(A): \blacksquare CH₂-CH₂ \blacksquare and

(C) Of a small quantity, preferably it is a α - olefin unit of 0.1-5 mol %:

(R ' expresses number of carbon atom 1 - ten alkyl groups.) And

(B) The next expression (I)

(during a ceremony, R expresses linear alkylene group more than number of carbon atom 4 X expresses the \cdot CH = CH₂ basis or the $\blacksquare\blacksquare$ basis.)

It is copolymer including the unit that it appears, and is expressed, and 0.2-20 mol % contains a unit (B) (B), higher than 1% of radical X of a unit relate to ethylene copolymer containing epoxy function in end of the side-chain which is $\blacksquare\blacksquare$ radical.

As mentioned earlier, copolymer of the present invention is constructed as from the unit that 0.2-20 mol % of a monomeric substance chain is expressed in $\blacksquare\blacksquare$ (B) , therefore, remaining 99.8-80 mol %, substantially (A), ethylene unit, it is constructed as from α - olefin unit with ethylene unit (C) (A).

In addition, more than 1% of basis X of a unit are epoxy function $\blacksquare\blacksquare$ in copolymer of the

present invention (B), and it is followed, and staying is $\cdot \text{CH} = \text{CH}_2$ radical, but even if it is contaminated with radical other than drop doing vice-life by a case in epoxidation reaction of unsaturation copolymer, for example, to be described below in a synthesis process of copolymer, there is not interfering.

A range of preferred molecular weight of copolymer of the present invention is 300-500000 2,000-200,000 in particular in number average molecular weight.

In addition, melt index value of copolymer (190 degrees Celsius, load 2.16kg) is for 0.001-5,000g/10.

For example, in copolymer of the present invention, number of carbon atom 1 - ten normal chain - branched chain alkyl group can give methyl group, ethyl group, propyl group, butyl group, a hexyl group, octyl radical, isopropyl group, two - carbonyl propyl group, the third butyl group, 2,2- dimethylbutyl radical for alkyl group R' of α - olefin unit ■■.

In addition, (B) preferably butylene radical, hexylene radical, octylene radical or decylene radical can be given for linear alkylene group more than number of carbon atom 4 of a unit.

Copolymer of the present invention,

(a) An ethylene unit: ■ $\text{CH}_2\text{-CH}_2$ ■, or

(a) An ethylene unit: ■ $\text{CH}_2\text{-CH}_2$ ■ and (c) a little α - olefin unit:

(R' expresses number of carbon atom 1 - ten alkyl groups.) And

(b) The next expression (II)

(during a ceremony, R expresses normal chain alkylene group more than number of carbon atom 4.)

Because epoxidation does 0.2-20 mol % higher than 1% of terminal unsaturation radical of side-chain of unsaturation copolymer to contain, linear α which it appears, and is expressed, ω nonconjugated diene units can be produced.

Unsaturation copolymer uses method and apparatus same as production of olefin polymer using so-called coordination catalyst, and it can be produced.

There is a method of Japanese Patent Application No. 2-18478 concerning an application of a this application person as an example of such a method.

α of the linear which is more than ethylene including ethylene or a little α - olefin and number of carbon atom 8 in this method, ω nonconjugated diene

[1]

[A] ヒドロポリシロキサン and reaction product with Grignard chemical reagent, it is extended

[B] The magnesium which it is responded as required raw materials ingredient, and was provided and a titanium component catalyst component invite titanium compound of the quaternary which is general formula $\text{Ti}(\text{OR})_n\text{X}_{4-n}$ (R, hydrocarbon group of $\text{C}_1 - \text{C}_{12}$, X, halogen atom and $0 \leq n \leq 4$)

[2] Organoaluminum compound

Preferably, more than existence bottom of a かなる catalytic substance, 50 degrees

Celsius, unsaturation copolymer is produced by existence bottom of absence of solvent or inert hydrocarbon solvent, normal pressure - 200kg/cm² making preferably do copolymerization under pressure of 3-30kg/cm² in temperature more than 130 degrees Celsius.

For example, number of carbon atom 3 - 12 α - olefin can give propylene, butene -1, pentene -1, hexene -1, octene -1, three - carbonyl - butene -1s, three - carbonyl - pentene -1s, four - methyl pentene -1s, 3,3- dimethyl - butene -1s, 4,4- dimethyl - pentene -1s, three - carbonyl hexene -1s, four - carbonyl - hexene -1s, 4,4- dimethyl - hexene -1s for α - olefin, preferably the quantity is based on unsaturation copolymer, and it is 0.1-5 mol %. In addition, 1,7-octadiene, 1,9- decadiene, 1,11- dodecadiene, 1,13- tetradecadiene can be nominated for α of the linear that carbon number 8 is older than, ω nonconjugated diene, the quantity is based on unsaturation copolymer, and it is 0.2-20 mol %.

A range of preferable ϕ molecular weight of unsaturation copolymer is 300-500000 2,000-200,000 in particular in number average molecular weight. In addition, melt index value of the copolymer (190 degrees Celsius, load 2.16kg) is for 0.001-5,000g /10.

For a method to introduce epoxy function into unsaturation copolymer, most general a method by the oxidation of olefiny unsaturated bond , in a specific example,

1. The oxidation by peroxy acid such as performic acid, peracetic acid, perbenzoic acid,
2. In vanadium, molybdenum, an existence bottom of catalytic substances such as tungsten compound or a non-existence bottom, oxygenated water or the oxidation by organic hydroperoxide,
3. The oxidation by alkalescence oxygenated water,
4. An existence bottom of acetylacetonato complex and ボルフィリン complex of transition metal or the oxidation by sodium hypochlorite under non-existence is given.

In addition, as another alternative, a compound containing epoxy function in a molecule, a method, for example, to add glycidyl thiol compound to olefiny unsaturated bond can be adopted. For this case, one part of basis X or everyone becomes the radical which glycidyl chemical agent added to the - CH = CH₂ basis in a unit of an expression (I).

Epoxidation reaction takes place in the condition which melted the condition which made the state that dissolved unsaturation copolymer in solvent or solvent swell or unsaturation copolymer.

For used solvent, it is selected by aliphatic, alicycle group, carbon hydride of aromatic, halogenated hydrocarbon, ester, ether, ketone, carbon disulfide.

Preferably introduction of epoxy function is higher than 20% in particular more than 5% more than 1% of olefiny unsaturated bond in unsaturation copolymer.

Even if there is not always selectivity coefficient at 100%, if epoxy function is introduced substantially, product by side reaction is introduced, and it does not interfere either.

(an example)

Example 1

(1) Production of reaction product [A-1]

Di-isopropyl ether solution 800ml (a commercial article), n-butyl magnesium chloride, 1.34 mol) of n-butyl magnesium chloride are gathered in the glass reactor which drying, nitrogen substituted for the inside well beforehand, while stirring, while, at メチルヒドロポリシロキサ ン (about 30 centimeters degree of viscosity at 25 degrees Celsius Stokes) 80.5ml (S1, 1.34 mol) that blockaded end in trimethylsilyl group, keeping room temperature, after the drip which did drip in one hour, it continued being stirred for one hour, and reaction product [A] which was brown transparence was got.

After, in solution of provided reaction product [A], addition diluted n-heptane 500ml in this way, at room temperature, two-ethylhexanol [C] 1.34 mol were taken for one hour, and drip was done.]

After drip termination, distillation under reduced pressure is done in pressure force 120-240mmHg, distillation was able to sting one ■. It is diluted in n-heptane, a n-heptane solution of reaction product [A-1] of colorless transparence was got. The density of magnesium is 0.782 mol/l.

(2) A catalyst component

[1] 10mmol gathered methylcyclohexane 77.7ml and reaction product [A-1] provided in (1) in magnesium standard in the の preparation glass reactor which drying, nitrogen substituted for the inside beforehand. While stirring, tetra-n-butoxy titanium [B] 0.5mmol which made methylcyclohexane dissolve is added at room temperature, it heated at 70 degrees Celsius for one hour. It cooled off in room temperature, and, after reaction termination, magnesium and titanium component catalyst component [1] were got.

(3) Inter-polymerization with ethylene and nonconjugated diene

Agitator, the catalytic substance which drying, ethylene substituted for the inside teach product made in stainless autoclave of internal space 1.2l that possessed a resist pressure container for cocatalyst supply methylcyclohexane 560ml and 1,9-decadiene (a product made in shell chemistry) 50ml (37.5g), it rose. 0.1kg/cm² introduce hydrogen at a point in time when 80 degrees Celsius were arrived at, catalyst component [1] which got diethylaluminum chloride [2] in 1.2mmol, (2) it amounted, and to mention above through attached resist pressure vessel at a point in time when temperature arrived at 148 degrees Celsius were introduced by 0.4mg each ethylene pressure in Ti conversion.

After having raised temperature to 150 degrees Celsius, while introducing ethylene continually so that total pressure becomes 8kg/cm² (hydraulic line pressure), it polymerized for one hour. After polymerization termination, polymerization was stopped in methanol including stabilizer イルガノツクス 1076.

Produced polymer is just divided, a polymer of 93.4g was provided when it dried. As for this ethylene-nonconjugated diene copolymer, as for number average molecular weight 23.000 by gel soft-headed mi A Chillon chromatography (GPC method), end vinyl cardinal number 1000 by an infrared absorption spectrum method (IR method) was 9.9 per carbon atom.

Example 2

Copolymerization reaction with ethylene was done in example 1 and a controlled condition except that 1,13-tetradecadiene (a product made in shell chemistry) 80ml were used as nonconjugated diene. Ethylene - non-conjugate decadiene copolymer of 63.0g is provided, number average molecular weight was 35,000, and, as a result of analysis, end vinyl cardinal number 1000 was 8.5 per carbon atom.

Hydro-extracting dry toluene 50ml were put in example 1 agitator, reflux condenser and three shares of flasks comprising a nitrogen introduction pipe except oxygen. Subsequently complex ethylene - nonconjugated diene copolymer 0.4g (vinyl group component 0.3mmol equivalent amount), meta chloroperbenzoic acid 74mg (0.3mmol) are added by example 1, while stirring under nitrogen atmosphere, it rises, it was responded at 90 degrees Celsius for 48 hours. After, after reaction, having cooled contents to room temperature, it was spent by the end of methanol 200ml. Mouth otherwise does produced deposition, subsequently vacuum drying was done. Characteristic absorption of epoxy function appears to $1,260\text{cm}^{-1}$, $1,847\text{cm}^{-1}$, $1,837\text{cm}^{-1}$ when the structure is analyzed by IR method about provided property modification copolymer in this way, the epoxy function conversion ratio was equivalent to 28.2 mol % of vinyl group before reaction. In addition, content 1,000 of vinyl group were 6.6 per carbon atom. An infrared absorption spectrum of this copolymer is shown to FIG. 1. In addition, extra, generation of epoxy function was confirmed by a nuclear magnetic resonance spectrum method (^{13}C -NMR method).

Example 2

When it was used in example 1, molybdenum hexacarbonyl 10mg (0.04mmol), disodium hydrogenphosphate 15mg (0.1mmol) were added to same ethylene - nonconjugated diene copolymer 0.4g, and it was preferable, and it was stirred. After it raised temperature, and having made provided solution 90 degrees Celsius, t-ブチルヒドロパーオキシド 0.5ml (5mmol) were stirred for drop giving, five hours, and it was responded. After reaction, product is processed same as example 1, property modification copolymer was got. 30.7 mol % of vinyl group before reaction changed in epoxy function when this property modification copolymer was analyzed by IR method.

Example 3

Epoxidation responded same as example 1 except that example 1 and similarly complex number average molecular weight 4,700, ethylene - decadiene copolymer of vinyl group content 9.5 were used as raw materials copolymer. As a result of analysis, the conversion ratio to epoxy function of vinyl group in copolymer was 30.2 mol %.

Example 4

Epoxidation responded same as example 1 except that complex ethylene - tetradecadiene copolymer was used as raw materials copolymer by example 2.

The conversion ratio to epoxy function of vinyl group was 25.4 mol % when property modification copolymer provided by IR method was analyzed.

(an effect of the invention)

Epoxy function component copolymer of the present invention owns epoxy function on the branched chain end that diverged from polymer backbone. For example, as for this end epoxy function, other compounds can be superior to reactivity with basic compound such as amine compound or amine group component polymer as compared with epoxy function in the inside of carbon chain. Thus, copolymer of the present invention is used using various reactivity and characteristic properties to come from this epoxy function by various resin material and resin degeneration material field of application. In addition, property modification, property modification can be used as material to be able to leave to a functional polymer having tall handloom ability.

By way of example only, copolymer of the present invention,

① It is useful as adhesive property resin so that adhesive force with various materials including metal such as steel, aluminum can be superior.

② 秀れた character is shown as binder with the resin which it is untied, and have functional group with epoxy function and reactivity of resin of non-compatibility, polyolefin resin in particular and polyamide and polyester · phase compatibilization agent mutually.

③ Various inorganic fillers and chemical combination are formed or because affinity is good, when it was used as an inorganic filler component resin composition, improvement of hardness of machine brings physical property improvement effect.

④ By polyamine or cross linkage agent such as polycarboxylic acid, leave cross linkage, and superior resin of physical property of machine having three dimension network structure can be converted to. In addition,

⑤ Reactivity of epoxy function is utilized, by photosensitivity, ion ligating property · the thing that exchangeability, antioxidation characteristics, chemical agent having various functional group such as biocompatibility · polymer is introduced into, it can be guided to photopolymer, ion-exchange resin, oxidation inhibitor, a medical high polymer.

4. brief description of drawings

FIG. 1 is an infrared absorption spectrum of copolymer of an example of the present invention.